>C=C: of the carbene. (The H_2C_3 results, of course, show significant energy differences between cumulene and methylene carbene forms.) As a further test of this qualitative carbene formation energy independence, the structure of transoid bivinylidene was optimized at the DZ/SCF level: R_{CH} = 1.077 Å, $R_{C=C}$ = 1.320 Å, R_{C-C} = 1.470 Å, ∠CCC = 125.7°, and ∠C-C-H = 119.8°. The DZ/SCF energy of this is −152.3265 au or about 83.5 kcal above diacetylene. This is roughly twice the vinylidene-acetylene energy difference, again suggesting that the energy to form a cumulene carbene has only a small dependence on the rest of the molecule's structure.

Dipole moments for the cumulene carbenes are given in Table V. In agreement with Hehre et al.[14] we find a dipole moment for propadienylidene of around 4 D. Interestingly, correlation effects on the dipole moment are small, which is in part due to the dominance of the SCF reference configuration in the correlated wave function. The dipole moment for butatrienylidene is almost the same as for propadienylidene. The stabilization of a cumulene carbene through charge separation proposed by Hehre et al.[14] for H_2C_3 and represented

$$\underset{H}{\overset{H}{>}}C^+ \!\!-\!\! C \!\!\equiv\!\! C^-$$
i
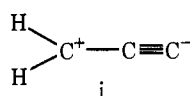
as i is most favorable when there is an odd number of carbons in the cumulene system. Thus, the dipole moment changes significantly in going from vinylidene to propadienylidene and likewise may be expected to change when going from H_2C_4 to H_2C_5.

Finally, presented in Figures 2a–f are the highest a_1 and b_2 occupied orbitals for the three cumulene carbenes.[15] Some preliminary idea of rearrangement barriers may be obtained by examining the nodal structures of the orbitals. For vinylidene, there is a node in the a_1 orbital perpendicular to the carbon axis around the methylene carbon, but there is no node for the b_2 orbital. The barrier for moving one of the two vinylidene hydrogens toward the other carbon is 8.6 kcal.[1] For

both H_2C_3 and H_2C_4, the highest b_2 orbital is the $2b_2$ and, unlike the vinylidene $1b_2$ orbital, there is a node around the methylene carbon. This suggests a larger rearrangement barrier for propadienylidene and butatrienylidene than vinylidene.

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An Amplified Sector Rule for Electric Dipole-Allowed Transitions[1]

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Abstract: A sector rule based on electron correlation or "dynamic coupling" between the chromophore and bonds of a molecule is developed for electric dipole-allowed transitions. In its simplest form, the development corresponds to a quantum model of rotatory strength arising from coupled electric dipole oscillators. With the rule, the sign and magnitude of transition rotatory strength can be estimated by examining a molecular model. Only knowledge of the transition wavelength and direction of polarization is required. Unlike most sector rules, it is necessary to observe carefully the orientation as well as the location of bonds placed dissymmetrically with respect to the chromophore. A number of illustrations are given for the butadiene 260-nm, the ketone 190-nm, and the ethylene 190-nm transitions. It appears that a "resonance" of the carbon–carbon bond polarizability perpendicular to the usually dominant polarizability along the bond occurs somewhere between 260 and 200 nm.

The Rosenfeld expression for rotatory strength:

$$R_{NK} = \text{Im}\{\boldsymbol{\mu}_{NK} \cdot \mathbf{m}_{KN}\} \tag{1}$$

defines the leading term, according to quantum mechanics, for the origin of optical activity in absorption band $K \leftarrow N$. The vector $\boldsymbol{\mu}_{NK}$ is the electric dipole transition moment and $\mathbf{m}_{KN}$

the magnetic dipole transition moment on going from state N to state K. The expression, correct to the dipole level of interaction between the light field and the molecule, is otherwise completely general. It assumes that molecular wave functions $|N\rangle$ and $|K\rangle$, with matrix elements that lead to suitably oriented dipoles $\boldsymbol{\mu}_{NK}$ and $\mathbf{m}_{KN}$, are sufficiently complete descriptions of the molecular system.

It is notable that the earliest models which detailed just how such dipoles could arise invoked the mechanism of "coupled electric oscillators".[2-4] In this mechanism the electric oscillator dipole μ_{NK}, largely localized in a part of the molecule and giving rise to a significant absorption of light at frequency ω_{NK}, "drives" another electric dipole oscillator in the molecule. The work of Kuhn especially[5] considered the juxtaposition required of two "coupled" oscillating electric dipoles within the molecule so that both molecular moments required by eq 1 would arise.

A later view accepted more widely at times, the "one-electron model",[6] was advanced primarily to dispute the notion that two oscillating electrons were the minimal requirement. Adherents to the one-electron model proposed that a single electron coupled to the static charge distribution in the molecule was a more likely origin of optical activity in the low-lying accessible absorption bands. The model was applied most readily to transitions strongly magnetic dipole allowed, transitions which were thus only weakly allowed in the electric dipole. The concentration on models for magnetic dipole-allowed transitions, and hence weak absorption bands, continued when it became apparent from Tinoco's work,[7] and the developments leading from it,[8] that electric quadrupoles (and higher multipoles) also act as the "driving" electric oscillator in an extended theory of coupled oscillators. Indeed, some general descriptions of optical activity in weakly absorbing bands recognize simultaneous contributions from one-electron and coupled oscillator mechanisms.[9]

The earlier theoretical emphasis on the study of $K \leftarrow N$ transitions with strong electric dipole-allowedness gave way also to obvious experimental practicalities. The condition of having a large anisotropy factor:

$$g_{NK} = 4R_{NK}/D_{NK} \qquad (2)$$

where

$$D_{NK} = \mu_{NK} \cdot \mu_{KN} \qquad (3)$$

is conducive to instrumental detection of a differential of circularly dichroic absorbance that is typically small compared to the average of the absorbance. From the definition of R_{NK} (eq 1) and D_{NK} (eq 3) one can see that transitions primarily magnetic dipole allowed tend to have the larger values of g_{NK}. Thus the easiest measurements to make and, until recently, the preponderance of data on R_{NK} have been for transitions strongly magnetic dipole allowed. A common generalization is that a circular dichroism spectrum compared to the ordinary absorption spectrum shows enhancement particularly of the magnetic dipole-allowed transitions, often revealing states undetectable in the ordinary absorption.

With the more recent improvements in instrumental sensitivities for dichroic measurements there is a growing body of data for rotatory strengths of strong electric dipole-allowed transitions. Correlations between molecular structure and the chiroptical properties of such transitions should be as useful as those derived for magnetic dipole-allowed transitions, and qualified by the same concerns for vibronic coupling.[10]

Well-founded sector rules[11] have been quite useful in studies of circular dichroism. They provide generalizations that relate molecular structure to sign and magnitude of circular dichroism and remove the need for repeated recourse to detailed calculations. Indeed, they are probably the only theoretical construct which can be used in a broad survey of cases to establish whether or not a fundamental intramolecular coupling mechanism is important for the optical activity. Establishment of the coupling mechanism is important for itself in understanding molecular properties. Once established, a given mechanism can be applied to the theories of diverse phenomena, as well as to more detailed and complete quantum calculations of rotatory strength. No sector rules for strong electric dipole-allowed transitions have been proposed that utilize dynamic coupling in a general theory.

This work will sketch the form of a sector rule that promises to be widely applicable to electric dipole-allowed transitions. But it is apparent early on in the theory that it is necessary to amplify somewhat the ordinary idea of a "sector rule", that the mere location of matter about the chromophore determines rotatory strength. It is evident that the orientation and the anisotropy of matter at a point are important along with the location of that point. Nevertheless, it seems possible to keep the rule usable while yet well founded on theory. The sector rule is based on a quantum-mechanical development of the mechanism arising from coupled electric dipole oscillators. As such, it is completely independent of the symmetric point group of the chromophore. The only knowledge of the chromophore transition that is required is the polarization of the $K \leftarrow N$ transition electric dipole and the approximate wavelength of absorption.

The information on molecular structure from the sector rule can also be based on data from natural circularly polarized luminescence.[12] In contrast to the structure for the electronic ground state that conditions the circular dichroism of the absorption process, it is the structure characteristic of the electronic excited state that yields the circular polarization of luminescence.

In the case of fluorescence the sector rule should be based on a strong electric transition dipole matrix element connecting two participating singlet states, the same transition dipole important to the absorption circular dichroism. In the case of phosphorescence, however, even what type of sector rule should apply can be uncertain. Spin–orbit coupling may introduce a state perturbing the electric transition dipole that is different from the state perturbing the magnetic transition dipole.[13] On the other hand, well-founded sector rules may serve to delineate a specific mixing among several alternatives when a number of experimental examples become available.

Theory

We consider a basis set $|A_r B_s\rangle$ consisting of the product of spectroscopic state real wave functions of chromophore $|A_r\rangle$ and of a single perturber $|B_s\rangle$. No electron exchange and negligible differential overlap between the chromophore and perturber are assumed. A perturbation V is the electrostatic energy of interaction between the chromophore and perturber charge distributions. The chromophore transition is taken to be strongly electric dipole allowed, essentially magnetic dipole forbidden, and corresponds to an $m \leftarrow 0$ transition of the isolated chromophore A. It has been shown[8] (also, see the Appendix) that then the first nonvanishing terms for μ_{NK} and $\mathbf{m}_{KN}$ are:

$$\mu_{NK} = \langle A_0 B_0 | \mu | A_m B_0 \rangle = (A_0 B_0 | \mu | A_m B_0) = \mu_{0m} \quad (4a)$$

$$\mathbf{m}_{KN} = \langle A_m B_0 | \mathbf{m} | A_0 B_0 \rangle$$

$$= \sum_j (E_m + E_j)^{-1} (A_m B_j | V | A_0 B_0)[(\pi i E_j/hc)\mathbf{R} \times \mu_{0j}]$$

$$+ \sum_l (E_m - E_l)^{-1} (A_0 B_l | V | A_m B_0)[(\pi i E_l/hc)\mathbf{R} \times \mu_{0l}] \quad (4b)$$

The energies E are relative to the electronic ground state of the chromophore (index m) or of the perturber (indexes j and l). It has been assumed that the perturber B is nonpolar so that any terms corresponding to a one-electron mechanism[8,9] can be neglected. Only dynamic coupling terms have been retained. Also it has been assumed that transition magnetic moments localized in the perturber and referred to an origin in the perturber are small compared to "Kirkwood terms" arising from transition electric moments μ_{j0} in the perturber displaced by
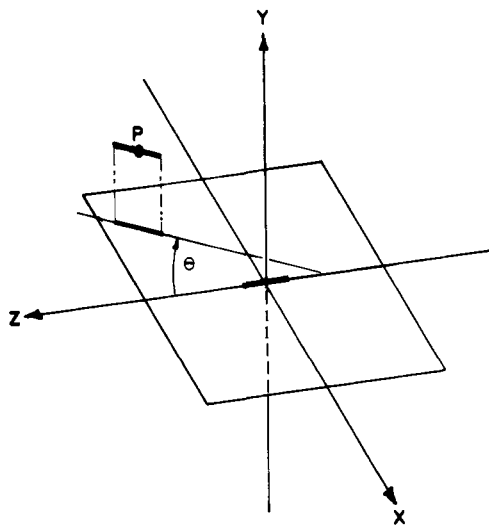
Figure 1. An orientation of the dipole polarization of a chromophore transition and the optic axis (see text) of a perturber so that the sectors of Figure 2 may be applied. In general, the transition dipole polarization must be centered at the origin and directed along the Z axis. The perturber must be rotated about the Z axis until its optic axis (e.g., a "bond" axis) is parallel to the XZ plane (i.e., perpendicular to the Y axis). $P = P(X,Y,Z)$ is the center of the perturber, to be located on each of the two parts of Figure 2. An angle θ is formed between the projection of the optic axis on the XZ plane and the Z axis. A positive angle θ is shown. A negative angle would correspond to counterclockwise rotation of the optic axis looking down the Y axis toward the negative direction.

R from the chromophore.[14] Expanding the matrix elements of the potential V and rearranging, eq 1 becomes:

$$R_{NK} = |\mu_{0m}{}^Z|^2 R^{-5} \sum_l 2E_m$$
$$\times (E_l^2 - E_m^2)^{-1}[3XZ\mu_{0l}{}^X + 3YZ\mu_{0l}{}^Y$$
$$+ (3Z^2 - R^2)\mu_{0l}{}^Z](\pi E_l/hc)(X\mu_{0l}{}^Y - Y\mu_{0l}{}^X) \quad (5)$$

The rotatory strength R_{NK} constructed from a dynamic coupling model is independent, to first order, of the origin to which angular momentum is referred.[8] Hence **R** has been taken conveniently to be a vector directed from the chromophore at the origin to the perturber. Initially, the components of **R** as well as those of the dipole vectors refer to a single coordinate frame oriented arbitrarily except that μ_{0m}, the chromophore transition dipole, lies along the Z axis. Upon referring the perturber moments to another coordinate frame centered on the perturber with its Z' axis along an "optic" axis and then averaging to cyclindrical symmetry about that axis,[8] the rotatory strength becomes:

$$R_{NK} = (\pi/hc)R^{-5}E_m[\tfrac{3}{2}Z(Y^2 - X^2)\sin^2\theta\sin^2\chi$$
$$-\tfrac{1}{2}X(R^2 - 3Z^2)\sin 2\theta\sin\chi - \tfrac{1}{2}Y(R^2 - 3Z^2)$$
$$\times \sin 2\theta\cos\chi - 3XYZ\sin^2\theta\cos 2\chi]$$
$$\times \bar\alpha(\nu_{0m})\beta(\nu_{0m})|\mu_{0m}{}^Z|^2 \quad (6)$$

where the polarizability definitions

$$\alpha_\| = \alpha_{Z'Z'} = \sum_l 2E_l(E_l^2 - E_m^2)^{-1}|\mu_{0l}{}^{Z'}|^2$$

$$\alpha_\perp = \alpha_{X'X'} = \alpha_{Y'Y'} \quad (7)$$

and

$$\bar\alpha = \tfrac{1}{3}(\alpha_\| + 2\alpha_\perp) \quad (8)$$

have been applied. $\beta(\nu_{0m})$ is a measure of the anisotropy of perturber polarizability:

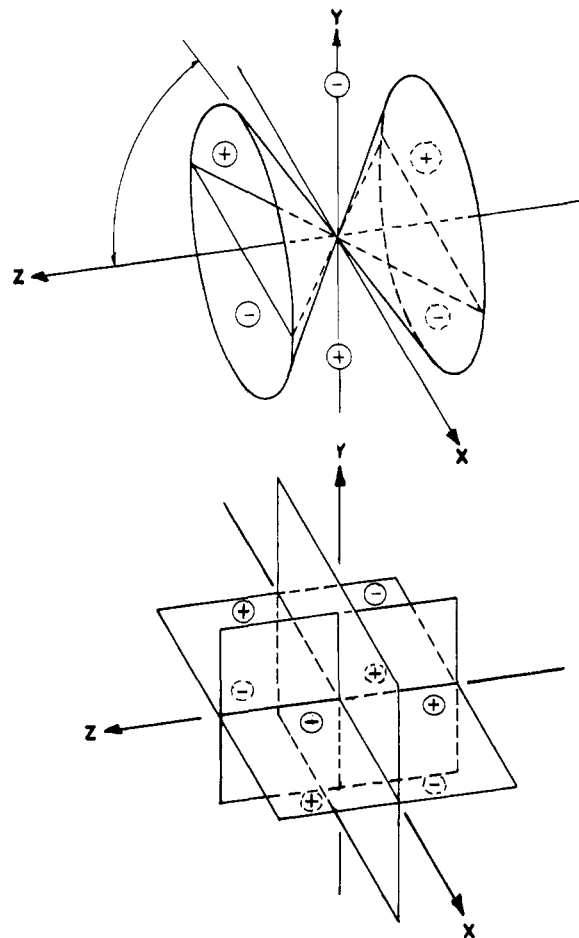$$\beta = 3(\alpha_\| - \alpha_\perp)/(\alpha_\| + 2\alpha_\perp) \quad (9)$$

Figure 2. Sectors and nodal surfaces for the two terms of eq 10. The signs refer to the *absolute* sign of rotatory strength when the trigonometric functions and $\bar\alpha\beta$ are all positive and $P = P(X,Y,X)$ (Figure 1) falls in that sector. The chromophore and perturber must be oriented in a manner illustrated in Figure 1 and more generally defined in that caption.

All are measured at the frequency of the $m \leftarrow 0$ chromophore transition. The Eulerian angles θ and χ are defined in ref 15.

One final coordinate transformation simplifies the form for the rotatory strength. It is always possible to view the juxtaposition of chromophore and perturber so that the angle χ is zero. That is to say, it is always possible to rotate the molecular system about the Z axis, i.e., about the chromophore electric dipole transition moment μ_{0m}, until the axis of cylindrical symmetry in the perturber (i.e., the optic axis) is parallel to the XZ plane (see Figure 1).[16] Then (6) reduces to:

$$R_{NK} = (\pi/hc)R^{-5}E_m[\tfrac{1}{2}Y(3Z^2 - R^2)$$
$$\times \sin 2\theta - 3XYZ\sin^2\theta]\bar\alpha(\nu_{0m})\beta(\nu_{0m})|\mu_{0m}{}^Z|^2 \quad (10)$$

The first and second terms are additive contributions to rotatory strength from a single perturber, contributions that have the nodal surfaces shown in Figure 2. The two functions of perturber coordinates in (10) transform as different irreducible representations of $D_{\infty h}$ or $C_{\infty v}$; thus no further simplification is possible.

It is important to notice that eq 10 yields *absolute* signs for rotatory strength. Thus a number of conventions should be observed carefully. The angle θ is measured between the axis of the chromophore dipole moment μ_{0m} (Z axis) and the projection on the XZ plane of the optic axis of the perturber as shown in Figure 1. A positive angle is defined by clockwise rotation, a negative angle by counterclockwise rotation of the optic axis looking down the Y axis in the direction of the negative coordinate. The coordinate frames are right-handed.

Table I. Comparative Characteristics of the Sector Contributions

	conical contributions	octant contributions
location-dependence	no contribution along space diagonals of the octants	maximal contribution along space diagonals of the octants
	maximal contribution along Y axis	no contribution along Y axis
θ dependence	modifies sign of contribution; positive factor for $0° < \theta < 90°$, negative factor $0° > \theta > -90°$	does not modify sign of contribution
	contribution vanishes for $\theta = 0°, \pm90°$; maximal for $\theta = \pm45°$	contribution vanishes for $\theta = 0°$, maximal for $\theta = \pm90°$
	contribution increases rapidly as θ moves from zero, decreases rapidly as θ approaches $\pm90°$	contribution increases slowly as θ moves from zero; decreases slowly as θ moves from $\pm90°$
general	origins of sectors located at the chromophore (see text, Figures 1 and 2). Location $P(XYZ)$ defined by the center of C–C bonds. Value of θ measured according to Figure 1. Contributions of C–H bonds neglected.	

Equation 10 in its simplest form represents the quantum mechanical model for optical activity arising from a pair of coupled electric dipole oscillators. This is particularly apparent when $\alpha_\|$ is defined by a single term of eq 7 while setting $\alpha_\perp = 0$.[9,17] The chromophore transition dipole μ_{0m}, which is largely responsible for the K $\leftarrow$ N absorption in question, then "drives" the dipole μ_{0l} of a perturber with a single $l \leftarrow 0$ transition.

It is noteworthy that the expression for rotatory strength of the $l \leftarrow 0$ "perturber" transition at frequency ω_{0l} with dipole μ_{0l} "driving" the $m \leftarrow 0$ transition oscillator of the former chromophore is simply:

$$R_{0l} = -R_{0m} \qquad (11)$$

This indicates a "couplet" of CD bands at their respective absorption frequencies, oppositely signed but carrying rotatory strength of equal magnitudes. The sign relationship can be laid entirely to the sign of the energy denominator in $\alpha_\|$. Both components of Figure 2 behave so that transferring the coordinate origin from "old" to "new" chromophore and rotating the frame to coincide with the transition polarization of the "new" perturber, thus reversing the sense of rotation and the sign of θ, have a combined effect that leaves the sign otherwise unchanged. Schellman[9] has called attention to the utility for theory in discerning couplet relationships between mutually perturbing transitions. However, it will become apparent that models limited to "one-transition" perturbers of the chromophore must be used with caution.

The magnitude of rotatory strength is directly proportional to the dipole strength of the chromophore transition $D_{0m} \approx D_{NK}$ (eq 3), or the oscillator strength:

$$f_{0m} = (2m_e/3h^2e^2)E_m D_{0m} \qquad (12)$$

Reporting values and variations of the anisotropy factor g_{NK} rather than rotatory strength R_{NK} would normalize data in a way that facilitates comparisons between different electric dipole-allowed transitions. Then such absorption data would also be readily comparable to the data normally obtained from circularly polarized luminescence.[12]

The perturber anisotropy $\bar{\alpha}\beta$ also has a direct influence on the magnitude of the rotatory strength. More importantly, it also affects the sign. A negative value for $\bar{\alpha}\beta$ indicates, for

example, that, in a one-transition model of the perturber, absorption of the perturber is at lower frequency than the chromophore absorption (cf. eq 7). However, this relation of perturber and chromophore absorption frequencies is not necessary for negative $\bar{\alpha}\beta$ when the perturber has more than one transition. A negative value of $\bar{\alpha}\beta$ can indicate merely that $\alpha_\| < \alpha_\perp$ (cf. eq 9). Each component of polarizability displays a dispersion with the frequency $\omega_{0m} = E_m/\hbar c$ of the inducing field, theoretically as given by eq 7, that affects the sign of $\bar{\alpha}\beta$. Thus the anisotropy and its sign at the frequency of the absorption ω_{0m} are required for applications of eq 10.

Details of an assignment of the chromophore transition, for example, to a particular electron promotion between molecular orbitals, are not required. A basic assumption, however, is that the chromophore is sufficiently small and symmetric so that electric dipole-allowedness and magnetic dipole-allowedness tend to be mutually exclusive. Even if strictly both are allowed in the appropriate representation of the chromophore point group, a transition electric dipole large in atomic units generally means that the corresponding magnetic dipole can be small if the origin of angular momentum for the chromophore is suitable chosen. The assignment of the transition or any one of several possible assignments by molecular orbitals usually can serve to illustrate this principle[18] for the case at hand.

Components of the Sector Rule. The two sets of nodal surfaces defining regional sectors (Figure 2) are applicable to the location P of a single perturber, with optic axis parallel to the XZ planes, relative to a chromophore located at the common origin. These two additive components may combine to form reenforcing or interferring contributions to the rotatory strength of the transitions. The sign of the contribution of one, the conical sectors, depends on the sign of θ.

Under many circumstances one component can be dominant, such as when the perturber lies on a nodal surface of the other component. In fact, it is a property of the two sets of sectors that a locus of positions giving maximum values of rotatory strength for a given value of R in one set of sectors corresponds to a node of the other set. Thus the space diagonals consisting of points $P(X,Y,Z)$, where $|X| = |Y| = |Z|$ so that the octant contributions are maximal, fall precisely on the conical nodes. Similarly, the locus of points $P(X,Y,Z)$ that constitute the Y axis and yield maximal conical contributions falls on an intersection of nodes of the octant sectors.

There are similar tendencies toward mutual exclusion of conical and octant contributions that depend on the angle θ defined in Figure 1. The contribution of conical sectors depends on the orientation of the perturber at a given point in the sector through the factor $\sin 2\theta$, the octant sectors through the factor $\sin^2 \theta$. These factors vary with θ as $2 \cos 2\theta$ and $\sin 2\theta$, respectively. Thus neither set of sectors contribute to optical activity if the optic axis of the perturber is parallel to the transition polarization ($\theta = 0$),[19] but the contribution of the conical sectors will tend to dominate for small angles of $\theta < 45°$. The contributions of the octant sectors tend to dominate for large angles near $\theta = 90°$. For θ exactly $90°$ the contribution of the conical sectors vanishes precisely. Table I summarizes these angle-dependent characteristics as well as those dependent on location of the perturber.

It seems meaningful to relate the signs for rotatory strength associated with the conical sectors to the sense of helicity between chromophore and perturber. Following the IUPAC proposal,[20] sense of helicity is defined unambiguously when μ_{0m} of the chromophore lies on the helix axis and the (extended) optic axis of the perturber is viewed as a tangent to the helix. In this definition, the helical sense is preserved even if the roles of a one-transition perturber and chromophore are interchanged. Adopting this view, the sense of helicity can be defined by the sign of θ: right handed for positive θ, left handed for negative θ, *if* one always orients the perturber to the upper
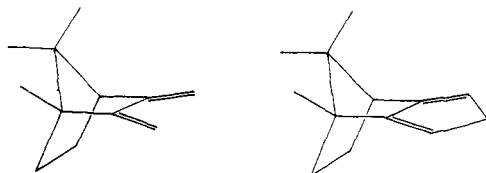
Figure 3. Two bornane derivatives (ref 24) with butadiene moieties that are chromophores for transitions near 260 nm.

$\Delta\epsilon_{252} = -0.6$ rel 24

Figure 4.

Figure 5. Sketch of a molecular model of (+)-2,3-dimethylenebornane (ref 24). A tetrahedral connector located at the chromophore center serves to define the location of the conical node in Figure 2. The angle indicated (also in Figure 2) is the angle formed by the cone surface and its axis, i.e., one-half the tetrahedral angle (~54° 44').

hemisphere in Figure 1 and measures the acute angle of the intersection. Maximum contribution of helicity to rotatory strength for a given perturber location occurs at $\theta = \pm 45°$.

A simple general rule for the contribution of helicity emerges. A *right-handed helix* (or, perhaps, a *left-handed skew*; see ref 27) contributes toward a *negative* rotatory strength when the perturber has $\bar{\alpha}\beta > 0$ and lies outside the cones. This corresponds to a classical helix model[21] which also yields negative rotatory strength for right-handed helicity. An exception is for placement within one of the solid angles subtended by the cones, constituting $(1 - (1/3)^{1/2})$ or about 0.42 of the 4π steradians subtended by a complete spherical surface. This anomaly relative to classical behavior is clearly related to the relative phasing of the oscillators determined by their interaction through V.

It is tempting to describe the signs of rotatory strength associated with the octant sectors as "anti-octant" (or "dissignate") compared to the usual representation of the ketone octant rule.[11] But signs associated with an octant rule depend on the conventions of orienting the chromophore-perturber system. A horizontal molecular plane of the ketone *chromophore* is conventional for its 300-nm octant rule;[22] a horizontal optic axis of the *perturber* has been taken as the convention in Figures 1 and 2. The only essential characteristic of the chromophore in Figure 1, a dipole moment, does not alone define a plane to be oriented. A "vertical" convention for the perturber, on the other hand, would bring the octant signs to coincidence with those of the ketone rule.

There is a meaningful difference in predicted R dependence: generally R^{-4} for the dynamic coupling model of the ketone octant rule, a much slower falloff with perturber distance R^{-2} for eq 10. For comparison consider a ketone $n \rightarrow \pi^*$ (300 nm) transition with $i\theta_{0m}{}^{XY}m_{m0}{}^{Z}$ large in atomic units,[11d] $\sim 5 \times 10^{-46}$ cgs unit and some dipole-allowed transition (for comparison, also at 300 nm) with $|\mu_{0m}{}^{Z}|^2$ also moderately large in atomic units, ~ 2.5 D^2 or 2.5×10^{-36} cgs unit. If each transition couples with a polarizable perturber located 2.4 Å away (corresponding to an axial C–C group in a substituent at the 2 position in cyclohexanone), the theoretical ratio of rotatory strength arising from the respective octant sectors is about 5. However, the bias toward stronger rotatory strength in the magnetic-allowed transition falls off with distance to a ratio of 2.5 if the perturber is located 3.6 Å away, the ratio approaching unity near 5.4 Å, a value typical of the distances between components of adjacent rings of steroids. Electric dipole transitions that are ten times more intense are known. Then the ratios are all reduced to one-tenth of the values above.

Applications

The rule will be illustrated for three chromophores that have well-characterized absorbing regions, that is, regions with known polarization, if not assignment, that are free from interfering overlap with other transitions. These are the inherently symmetric moieties of butadiene, ethylene, and the carbonyl group of ketones.

Butadiene. The butadiene chromophore in its planar cisoid form is characterized by a long-wavelength transition with
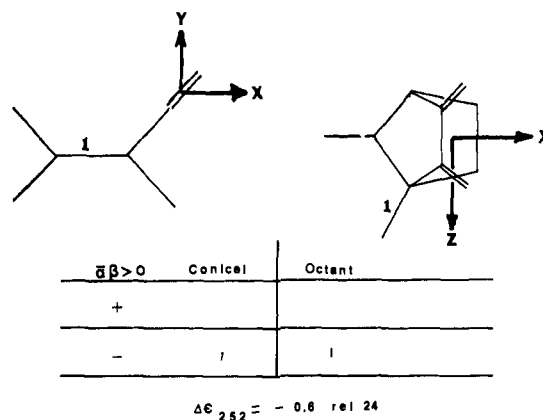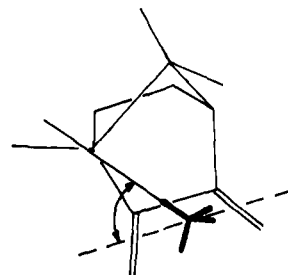
λ_{max} near 260 nm and ϵ_{max} about 3300 in cyclohexane solvent.[23] Its dipole strength D_{NK} is approximately 4.6 D^2, corresponding to moderately strong dipole-allowedness a dipole of 1-Å length with charges about one-half of the electronic charge. It has been assigned uniformly in the literature to the $\pi_2 \rightarrow \pi_3^*$, $^1B_2 \leftarrow {}^1A_1$ (in plane, C_{2v}) transition.

Two compounds synthesized by Burgstahler and co-workers[24] provide an excellent opportunity to illustrate eq 10, the rotatory strength arising in this instance from the transition dipole of the planar diene chromophore coupled to the anisotropic dipole polarizability of a "single perturber" The molecular structures given in Figure 3 represent cases where the activity arises from the substitution of one bridgehead C–H group by a C–CH$_3$ group. To the extent that the pyramidal tetrahedral structure of the CH$_3$ group as directed is equivalent in its anisotropy $\bar{\alpha}\beta$ to one C–H group directed along the same axis, the substitution is the equivalent of introducing one anisotropic C–C "bond". For our purposes now we consider it to be centered at a "mean" position, at the methyl carbon.

We proceed to analyze the rotatory strength as shown in Figure 4. With the aid of molecular models and Figure 5 it is not hard to verify that bond 1 lies inside, but very near a conical nodal surface. Viewing first its position in the conical sectors of Figure 2, then noting the angle θ according to Figure 1, and finally considering the sign of $\bar{\alpha}\beta$, a very weak negative contribution is predicted, indicated by / in the "conical" column. While reasonably far from the octant nodal surfaces, the angle of θ is not large and only a moderately small contribution, also negative and indicated by 1, is expected from that part of eq 10. In fact, the angle θ differs from zero just to the extent that the methylene bridge of the six-membered ring distorts regular tetrahedral angles of the bonds. A very weak negative circular dichroism near 260 nm is predicted.
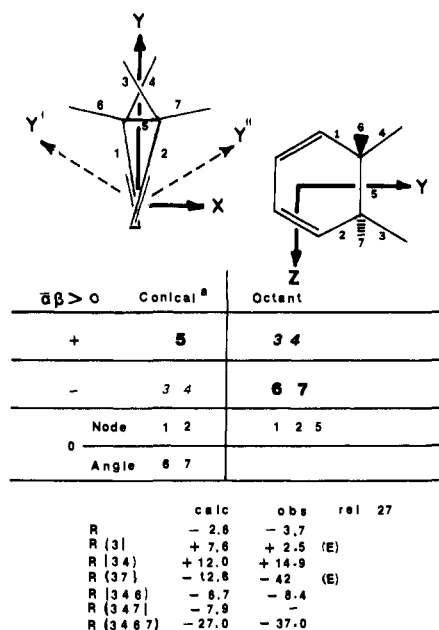
$\bar{a}\beta > 0$	Conical[a]	Octant
+	5	3 4
−	3 4	6 7
0 Node	1 2	1 2 5
Angle	6 7	

	calc	obs	rel 27
R	− 2.6	− 3.7	
R (3)	+ 7.6	+ 2.5	(E)
R (3 4)	+ 12.0	+ 14.9	
R (3 7)	− 12.6	− 42	(E)
R (3 4 6)	− 6.7	− 8.4	
R (3 4 7)	− 7.9	−	
R (3 4 6 7)	− 27.0	− 37.0	

Figure 6. In this and all other tabulations, the type-form (e.g., **1**, *1*, 1, *l*) indicates the relative magnitude of bond contributions, from very strong (**1**) to very weak (*l*).

The sign of the anisotropy of polarizability $\bar{\alpha}\beta = (\alpha_\parallel - \alpha_\perp)$ for the C–C bond must be positive to give the observed sign of CD.[24] A positive value is consistent with nearly all reported measurements at static or very long wavelength fields.[25]

Several modifications of the chromophoric systems in Figure 3 have been reported along with their circular dichroisms. When both $C=CH_2$ groups of the butadiene moiety are replaced by $C=O$, the resulting dione also has a negative circular dichroism, $\Delta\epsilon_{222} = -1.3$.[24] If the absorption at 222 nm for a dione is analogous to the *cis*-butadiene absorption at 260 nm and there is no charge in sign of $\bar{\alpha}\beta$, one would expect the rotatory strength to be negative, as observed. It is not unexpected, on the other hand, that in cases where the two groups are different (i.e., $C=O$ and $C=CH_2$, or $C=O$ and $C=CHCO_2Me$, or $C=O$ and $C=CHOCH_2CH=CH_2$), thus leading to some reorientation of the transition dipole for that absorption region, different signs and magnitudes of circular dichroism can obtain. The result of such reorientation is that all parts of the bornanone frame contribute to the rotatory strength. For these cases, a strong positive circular dichroism has been observed.[24]

Before proceeding to examine in detail molecular dissymmetries that are more complex, we will adopt a number of assumptions: (1) that the rotatory strengths induced by more than one perturber are additive, (2) that the centers of C–C bonds define the position P shown in Figure 1 and to be located on the sectors of Figure 2, and (3) that C–H bonds have negligible anisotropy[25,26] and thus make no contribution to rotatory strength. These are not all entirely defensible from a theoretical viewpoint, but some experience shows them to be serviceable for a useful sector rule.

With the above assumptions, one may consider several alkyl-substituted 1,3-cyclohexadienes. The analysis can be compared to CNDO/S calculations by Rosenfield and Charney[27] where the cyclohexadienes are considered as models for certain steroids. The calculations are quite successful in predicting the rotatory strength observed for the corresponding steroids.

Two views are sufficient to make the analysis, each helpful for estimating conical and octant contributions. The arbitrary numbering system identifies C–C bonds. We note that the

CNDO/S calculations used a ring geometry that deviated from the C_2 symmetry shown in Figure 6. The coordinate axes X and Y indicate the orientation necessary to consider the placement of the center of C–C bond 5 in Figure 2; Y' shows the rotation around Z to consider 4, Y''' to consider 3. X and Y axes need to be rotated only slightly to consider bonds 6 and 7. Slight rotations of the X', Y' and X'', Y'' axes accommodate bonds 2 and 1. **R** refers to the rotatory strength of the unsubstituted cyclohexadiene, **R**(3) cyclohexadiene with substitutent 3, etc.

Disregarding for the moment inherent dissymmetry of the butadiene moiety, the rotatory strength predicted for **R** by eq 10 arises from a large positive conical contribution of bond 5. The large contribution of bond 5 arises from an optimal placement in the conical sectors together with a favorable value for θ, no more than 30°. With inspection of molecular models and use of Figure 5, the centers of bonds 1 and 2 are seen to be virtually on the conical nodal surface as well as the octant XZ nodal surface. The rotatory strength observed and calculated by CNDO/S contains an inherent dissymmetry contribution[27] calculated to be about -12.2 (for a left-hand skew sense of 14°). Thus the net contribution of bonds 1, 2, and 5 does seem to be positive and nearly equal in magnitude to the inherent dissymmetry of the butadiene moiety.

Bonds 3 and 4 make small conical contributions due to positions near both the conical node and the planar node. Large angles for θ near 60° enhance the octant contributions of opposite sign. Bonds 6 and 7 are optimally positioned and oriented for large negative octant contributions indicated by **6** and **7**, consistent with the allylic axial substitutent rule,[28] but a simple calculation shows that the conical contribution of bond 5 should be about as large as that of bond 6 or bond 7. There is remarkable agreement between the results of eq 10 and results from CNDO/S calculations. The reason for agreement is examined further in the Appendix.

Rosenfield and Charney report a fairly large magnetic transition dipole of 0.5 Bohr magneton for planar *cis*-butadiene when the origin is located at the midpoint of the bond connecting carbon atoms 2 and 3 of the diene. We can examine briefly whether this fact represents a breakdown of a key assumption in developing eq 10. At the same time the nature of the origin independence of first-order dynamic coupling expressions[8] will be clarified.

First we model the transition charge density of the chromophore by two opposed point dipoles. A large one, $\mu_{1,4}{}^Z$ is centered on the midpoint of a line connecting carbon atoms 1 and 4 of the butadiene moiety and directed along that line; another small dipole $\mu_{2,3}{}^Z$ is centered on the midpoint of a line connecting carbon atoms 2 and 3 and directed along that line in a sense opposed to the large dipole. Then it is easy to show that the symmetry allowed X-polarized magnetic dipole is given by:

$$m_{m0}{}^X = +(\pi i E_m/hc)(Y_{2,3}\mu_{2,3}{}^Z + Y_{1,4}\mu_{1,4}{}^Z) \qquad (13)$$

which vanishes with an appropriate choice of origin to which angular momentum is referred. That origin, in the moiety "plane", is nearest the larger dipole but located on the side opposite the smaller dipole. It is just such a choice of origin for such a chromophore transition charge density that is consistent with the expression of transition magnetic dipole given by eq 4b. To the extent that it does not differ significantly from the center of gravity of charge of the chromophore that defines the coordinates of the multipole expansion, it also represents the "convenient choice of origin" for eq 10.

Moving the origin back to the choice of Rosenfield and Charney gives a new term in the expression for R_{NK}, a term that depends on the presence of a significant transition magnetic dipole moment in the chromophore. The new term is the same as eq 9 of ref 8, except that a dipole–dipole potential is appropriate, giving:

$$R_{NK}' = -i\mu_{0m}{}^Z m_{m0}{}^X R^{-5} \sum_l 2E_l(E_l{}^2 - E_m{}^2)$$

$$\times [3XZ\mu_{0l}{}^X + 3YZ\mu_{0l}{}^Y + (3Z^2 - R^2)\mu_{0l}{}^Z]\mu_{0l}{}^X \quad (14)$$

The effect on eq 10 of such an origin change is most readily seen when it has the form of eq 5. The terms in square brackets derive from the potential V which is independent of origin. The last terms in parentheses are the origin-dependent magnetic dipoles to which we introduce new coordinates $\overline{Y} = Y + \Delta Y$, $\overline{X} = X$. With some rearrangement of terms, the change ΔR_{NK} in eq 5 from shifting the origin of angular momentum by ΔY becomes:

$$\Delta R_{NK} = +i\mu_{0m}{}^Z (\pi iE_m/hc)\Delta Y \mu_{0m}{}^Z$$

$$\times R^{-5} \sum_l 2E_l(E_l{}^2 - E_m{}^2)$$

$$\times [3XZ\mu_{0l}{}^X + 3YZ\mu_{0l}{}^Y + (3Z^2 - R^2)\mu_{0l}{}^Z]\mu_{0l}{}^X \quad (15)$$

If the magnetic dipole $m_{m0}{}^X$ is zero when ΔY is zero, then:

$$m_{m0}{}^X = +(\pi iE_m/hc)\Delta Y(\mu_{2,3}{}^Z + \mu_{1,4}{}^Z)$$

$$= +(iE_m/hc)\Delta Y \mu_{0m}{}^Z \quad (16)$$

and since on substituting (16) into (14) one has

$$R_{NK}' = -\Delta R_{NK} \quad (17)$$

the contribution of the new term is precisely cancelled by the change in eq 5 or, equivalently, eq 10. This is an example of the general origin independence of first-order dynamic coupling expressions for rotatory strength.

The relationship we have just illustrated can be discerned in the CNDO/S calculations.[29] There the projection on the X-polarized magnetic dipole, i.e., the coefficients to $m_{m0}{}^X$ in eq 14, closely parallels the projection on the Z-polarized electric dipole, i.e., the coefficient to $\mu_{0m}{}^Z$ in eq 5, as substituents are varied. Through the scalar products associated with these two moments have different signs, the changes introduced in each by substituents have the same sign. Thus the computational analog of eq 14 appears to be rather faithfully supplying to the computational analog of eq 5 or 10 the deficit created by an "arbitrary" choice of origin. This observation is important in that it suggests a precisely correct choice of origin in the chromophore is not important for a qualitative rule, probably as long as the R distances of eq 10 are large compared to the origin variations being considered. It reaffirms that terms like $\mathbf{R} \times \mu_{0l}$ (eq 4b) projected on μ_{0m} (eq 4a) are sufficient in form to describe the rotatory strength of substituted cyclohexadienes.

A closely related question is the effect on the validity of eq 10 from skewing the butadiene chromophore so as to be inherently dissymmetric. Skewing introduces in the chromophore X-polarized electric dipole and Z-polarized magnetic dipole transition moments. With a choice of origin that minimizes the magnetic dipole of the planar chromophore, the skew-induced magnetic dipole is only about 0.04 Bohr magneton for the 14.4° assumed in computations.[27,29] Such a small value allows one to use the lowest order of approximation for its contribution, whereby the contribution is simply additive. The effect of the X-polarized electric dipole induced by skew can be accommodated if desired by the choice of Z axis for eq 10. In the model of transition density that has been assumed, a rotation of the Z axis less than that which skews gives to the $\mu_{1,4}{}^Z$ dipole would be required.

An analysis of (+)-5α-androsta-14,16-diene[24] illustrates a case where generalized trends can be discerned that include all parts of the C-C skeleton in the steroid (Figure 7). In this case the coordinates shown are appropriately oriented for only the bonds 5, 6, 7, 8, 13, 15, and 16.

The bonds 6, 5, 13, 15, and 16 yield alternating values of conical contributions falling off, undoubtedly to negligible
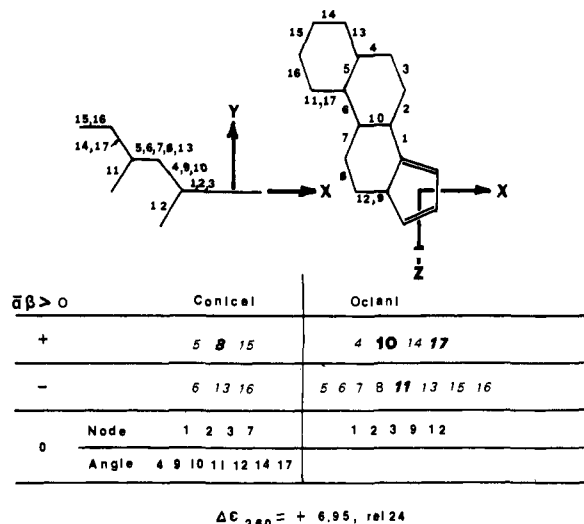

$\bar{a}\bar{\beta} > 0$		Conical	Octant
+		5 *8* 15	4 **10** 14 **17**
−		6 13 16	5 6 7 8 **11** 13 15 16
0	Node	1 2 3 7	1 2 3 9 12
	Angle	4 9 10 11 12 14 17	

$$\Delta \epsilon_{260} = + 6.95, \text{ rel} 24$$

Figure 7.

contributions in magnitude, with increasing distance and nearly cancelling. Bond 7 is on the conical node. Bond 8 is well positioned and oriented for a relatively large positive conical contribution.

The octant contributions of these same bonds are negative, but far from optimal for their positions in space owing to unfavorable angles of $\theta \approx \pm 35°$. These negative octant contributions are more than compensated by positive octant contributions from bonds 10, 4, 14 whose magnitudes of coordinate position (on a properly rotated set; see Figure 1) are each closely matched by coordinates of the former set of bonds, but have optimal angles. Since $\sin^2\theta$ is $\frac{1}{3}$ for the former and 1 for the latter, it is clear that the positive octant contributions will dominate. The contribution of bond 11 should cancel nearly precisely that of bond 17. The observed positive circular dichroism is then readily accounted for, a large degree of self-cancelling contributions not withstanding. When the C—C group of bond 4 is replaced by C=C, the circular dichroism changes from +6.95 to +7.54, consistent with an increase in $\bar{a}\bar{\beta}$ at that location.[24]

It is noteworthy that a large number of bonds make little or no contributions due to their angle of orientation with the transition polarization or their position on nodes. This includes, in the standard notation of the steroidal frame, the C-13 β-Me bond (bond 12 above) that is axial allylic to the 16–17 double bond. While positive sign of circular dichroism has been attributed previously to a chirality contribution from this interaction,[24] the present model, in contrast, yields no contribution from this group.

Ketone Carbonyl. The ketone chromophore is characterized by a transition in the ultraviolet immediately after the well-known 300-nm n $\rightarrow$ π^* band. It has λ_{max} from 185 to 195 nm in steroidal and other cyclic systems with $\epsilon_{max} \approx 1200$ for cyclohexanone and $\epsilon_{max} \approx 3000$ for cyclopentanone, both measured in the vapor phase. Thus the dipole strength is about 10.6 D^2 for cyclopentanone. The transition is assigned as n $\rightarrow$ σ^*_{CO} on the basis of a polarization corresponding to $^1B_2 \leftarrow {}^1A_1$ (in-plane, C_{2v}).[30]

Kirk, Klyne, and co-workers[31] have reported a large body of data for the circular dichroism of steroid ketones at 185–195 nm. They summarize the results by a slight modification of the familiar octant rule projection shown in the lower part of Figure 8. Though derived from systems where a large number of perturber interactions need to be considered, arguments they have made on differential effects allow us to consider the figure as giving the effect of a single methyl or methylene substituent.
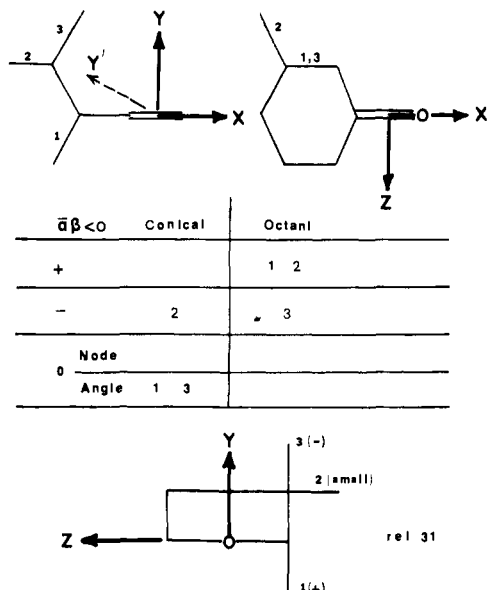
Figure 8.

Figure 9.

It is immediately obvious that the location and orientation (on X', Y', Z) of an axial C-C group α or β to the carbonyl group (e.g., bond 1 or bond 3) yield a contribution from the octant component alone. On the other hand, the equatorial substituent bond 2 has interferring (oppositely signed) contributions (referring to X, Y, Z) that account for the very small rotatory strength it induces.

It is easy to determine that neither of the two other possible electric dipole polarizations for the ketone transition yields the sign alternation for axial bonds, regardless of the sign given to $\bar{\alpha}\beta$, along with the interferring conical and octant contributions for the equatorial bond. It appears that no more than these generalized observations on the rotatory strength support the assigned polarization.[30]

One must take $\bar{\alpha}\beta < 0$ if the experimental data for absorption at 185 to 195 nm is to agree in absolute sign with (10). This is not unexpected in view of the spectroscopic properties of many diatomic molecules. For example, the first singlet excited states of the hydrogen halides (isoelectronic in the valence shells with methane) are $^1\Pi$; the first of F_2 (isoelectronic with H_3C-CH_3) is $^1\Pi_u$.[32] Therefore, the lowest $l \leftarrow 0$ singlet–singlet transition from the ground state is polarized perpendicular to the bond axis. It is reasonable that on approach to sufficiently short wavelengths such as 190 nm the contributions of states to the C-C bond polarizability (eq 7) can be dominated by such a low-lying perpendicular transition. There is direct experimental evidence in the absorption spectrum of ethane[33,34] that the perpendicular transition is weaker than the parallel polarized transition. Then (7) suggests that the perpendicular contribution to $\bar{\alpha}\beta$ at a sufficiently long wavelength, such as 260 nm for the butadiene chromophore or with static fields, will be minor relative to the parallel contribution. This is clearly so for a two-transition perturber with the properties assumed. An analysis of the rotatory strength associated with the ethylene chromophore, absorbing in the same spectral region, suggests the same "resonance" or "optical exaltation" in the dispersion of $\alpha_\perp$.

Ethylene. The ethylene chromophore in chiral systems has been the subject of intense study recently.[35-37] These studies clearly demonstrate the unique value of chiroptical techniques for making spectroscopic assignments, especially when used in conjunction with more traditional spectroscopy. The studies underscore the complexity in the absorbing region from 230 to 160 nm that arises from overlapping bands subject to considerable shift in frequency by individually varying degrees
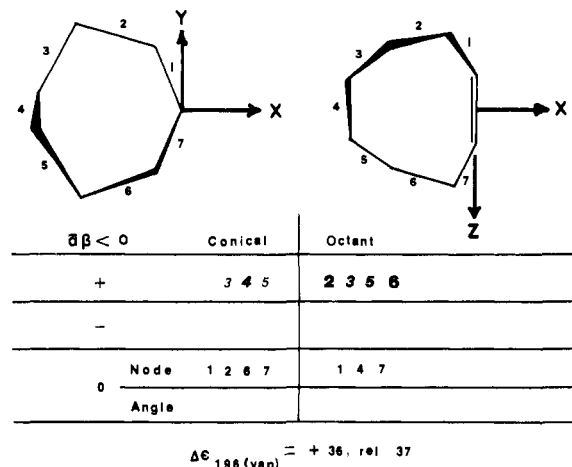
Table II. The $\pi \rightarrow \pi^*$ Transition in Methyl-Substituted Ethylenes[a]

no. of CH_3 groups	λ_{max}, nm
0	164
1	174
2(1,1)	186
2(1,2-cis)	175
2(1,2-trans)	178
3	184
4	188

[a] Adapted from ref 38.

upon substitution of the chromophore or modification of the solvent medium. It is now possible to assign and follow in various compounds with considerable certainty the long-axis polarized transition designated $(\pi \rightarrow \pi^*)$ $B_{1u} \leftarrow A_{1g}$ (D_{2h}). The absorption has a λ_{max} that depends on substitution[38] as given in Table II and a dipole strength in the range[35] of 4 to 14 D^2. In ethylene this transition appears to cover a quadrupole-allowed transition[39] that is observed at the next higher frequency in substituted compounds.[35-37] The frequency just below the $\pi \rightarrow \pi^*$ transition shows evidence of a weak $\pi \rightarrow 3s$ transition that is subject to large shifts, even exceeding the shifts of the other more prominent bands.[35,36]

The C_2 molecule (+)-*trans*-cyclooctene has been assigned the chair conformation in the vapor state, contrary to the results of determinations in the solid state.[40] An analysis for rotatory strength in the vapor is given in Figure 9. The coordinate system, indicating the transition dipole polarization, is otherwise arbitrary.

Bonds 2 and 6 lie on conical nodes when they are properly rotated about the Z axis. Bonds 3 and 5 make positive conical contributions, though weak, owing to a large angle θ as well as close proximity to a node. Bond 4 is ideally situated to make a large conical contribution, even with a small angle. The octant contributions of bonds 2 and 6 are probably dominant with their large angles, acting not unlike the allylic axial substitutents of cyclohexadiene. Bonds 3 and 5 are closer to nodes. Every contribution is for a positive rotatory strength, which is observed in the vapor.[37]

This analysis, or a similar one for the twisted (solid) conformation,[41] ignores the mixing of magnetic dipole allowedness into the $\pi \rightarrow \pi^*$ transition due to inherent dissymmetry of the ethylene chromophore.[35,42] It has been assumed that the mixed-in element is primarily π_x to π_y^* electron promotion[42] (in the coordinate system of the figure above). The effects

Table III. Characteristics of Chromophores and Perturbers

chromophore	λ_{max}, nm	polarization (Z axis)	$\bar{\alpha}\beta^a$
cis-butadiene	240–260	in-plane, long axis[b]	positive
ketone carbonyl	185–195	in-plane, perpendicular to C=O bond[c]	negative
ethylene	175–200	parallel to C=C bond[d]	negative

[a] For saturated hydrocarbon perturbers. Positive for chromophore absorptions at wavelengths of 260 nm and longer. Negative for chromophore absorptions at wavelengths of 200 nm and shorter, up to the absorption wavelength of saturated hydrocarbons. The wavelength between 260 and 200 nm where crossover from positive to negative occurs is not known at present. [b] Reference 23. [c] Reference 30. [d] References 35–38. Note that observation of the very intense ordinary absorption is necessary for distinguishing this band from several others in the same region.

Figure 10.

should be similar to that of skew in the chromophore of substituted 1,3-cyclohexadienes. In this case, no electric dipole is induced; the induced magnetic transition dipole is Z-polarized. The contribution to rotatory strength has been computed to be negative[42] for the absolute configuration shown here and thus does not appear to dominate. Scott and Yeh have come to the same conclusions concerning the greater importance of dynamic coupling contributions.[43] They also have found it necessary to assume $\bar{\alpha}\beta < 0$ to have agreement with experiment.

Another C_2 molecule, twistene, shows a large degree of self-cancellation of contributions (Figure 10). Only one coordinate orientation is shown. Other orientations are required.

Bonds 2 and 8 lie on the conical node, bonds 4 and 6 lie outside, but fairly near the cones giving positive contributions. The pairs 2, 4 and 6, 8 give contributions that are small due to near cancellation of octant contributions between the members of each pair. However, bonds 8 and 2 should dominate slightly. Bonds 3 and 7 give only conical contributions but are optimally positioned and oriented to give large positive values. Bonds 9 and 11 give moderate negative octant contributions; bond 10 is quite distant, giving a negative conical contribution. The observed circular dichroism is positive; it appears likely that the bonds 3 and 7 dominate to give the observed positive rotatory strength.

Comments and Conclusions

The analyses of molecular systems for rotatory strength by eq 10 are straightforward, utilizing a well-defined scheme summarized in Table III, along with Table I For many cases, prediction of the net, experimental value is devoid of any ambiguity. Even the effort applied to more complex cases can be rewarding. No more than a molecular model is required. The degree of success in predicting the sign of circular dichroism seems no less than for the ketone octant rule.[11a]

The amplified sector rule gives striking support to the concept of the allylic axial substituent rule as applied to both monoenes[44] and dienes.[23] It makes explicit that such formulations depend on specific properties of specific transitions, that substituents may not have to be immediately adjacent to the chromophore,[45] and that specific properties of the substituent also have specific effects. On the other hand, there is some indication that the role of allylic axial hydrogens has been overemphasized. CNDO/S calculations,[27] empirical compilations of bond polarizability components,[25] and Hartree–Fock computations of bond polarizabilities[46] support that indication.

The amplified rule displays another corollary that has not yet been recognized, a "helix-pair" rule. Such a rule is based on the optimal conical contribution when the optic axis of a
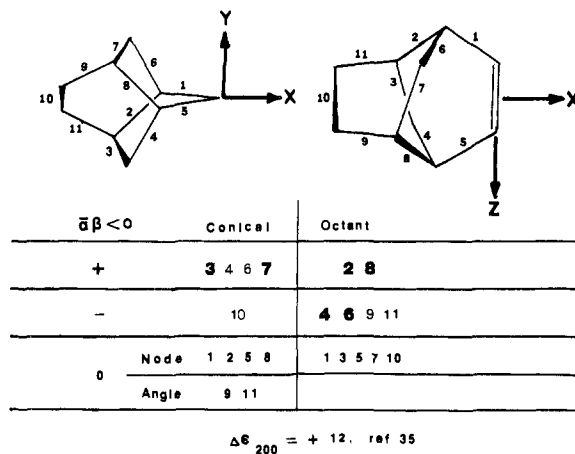
bond is paired to the transition polarization and lies near the Y axis of Figure 1, with θ defining a helix sense. Bond 5 in 1,3-cyclohexadienes, bond 4 in cyclooctene (chair form), and bonds 3, 7, and 10 in twistene all lie precisely on that Y axis, bond 8 nearly so in the androstadiene. When strong allylic axial substituent interactions are absent, helix-pair contributions may dominate the chiroptical properties of allowed transitions.

The viewpoints adopted here cannot provide any basis for the olefin octant rule.[47] That rule is derived from the symmetry arguments of a static coupling mechanism.[48] Nevertheless, an analysis with the amplified sector rule easily predicts, for example, that the 19-nor analog of a cholest-4-ene should show a positive increment in $\pi \to \pi^*$ rotatory strength because of the loss of the 19-methyl group. (The enantiomeric cholest-5-ene should show a decrease.) The 19-nor analog of cholest-6-ene can be expected to show a negative increment in rotatory strength owing to the loss of the methyl group. (Cholest-7-ene is enantiomeric and should show an increase on going to the nor alalog.) However, there appear to be no satisfactory data at this time for confirming these predictions since reliable spectral assignments, with few exceptions,[35,49] are lacking.

The set of working assumptions appear to be reasonably serviceable. Some modifications may become desirable such as, for semiquantitative analyses, a redevelopment of (10) using a charge-dipole expansion[8] instead of the dipole-dipole expansion. This would allow the transition density to be treated as a set of charges distributed over the chromophore. The allocation of polarizability anisotropy between C–C bonds and C–H bonds[26] may be important enough sometimes to require reconsideration. Also, strict additivity of perturber contributions to rotatory strength cannot be expected since any one perturber is modified by the presence of all other perturbers. In particular, there is very good reason to believe that polarizability anisotropy $\bar{\alpha}\beta$ will be affected to a degree much greater than will be the mean polarizability[50,51] that is more important for the ketone octant rule.[11d] In addition, there is good reason to believe that the "resonance frequency" of $\bar{\alpha}\beta$ for a perturber may be a function of intramolecular environment[51,34] to a degree that is significant in some cases.

Any of the above may be applicable to the case of α-pinene, barring an error in the assignment of absolute configuration.[52] The $\pi \to \pi^*$ rotatory strength of (−)-(1S,5S)-α-pinene, with a well-defined molecular conformation,[35] is anomalous in view of eq 10 and dynamic coupling calculations[43] when C–H contributions are neglected. An analysis by (10) reveals that only the bridgehead methyl C–C bond directed very near and over the double bond should make a contribution. That contribution is purely "conical" and clearly positive assuming $\bar{\alpha}\beta$

< 0; however, the rotatory strength for the $\pi \rightarrow \pi^*$ transition is negative.[37] All other bonds are either coplanar with the transition dipole or form an array with a plane of symmetry that includes the chromophore. The isomer $(-)$-$(1S,5S)$-β-pinene, on the other hand, is conformed more nearly like steroidal systems and many bonds make contributions. In this case the analysis via (10) unequivocally yields the positive rotatory strength that is observed.[37] Methods that deal with many of these limitations in a rigorous way are referred to in the Appendix.

Appendix

It may be surprising that applications of the CNDO/S method with*out* configuration interaction (CI) have yielded rotatory strengths[27] that parallel those from a perturbation method based on "electron correlation".[8] Significantly, the two methods also agree on the sign of the rotatory strength. Yet an inspection of the CNDO method[53] without CI confirms that it does not include explicitly any of the electron repulsion integrals that are identified with "dynamic coupling".

One can see that the parallel behavior arises in a large measure from the nature of the magnetic dipole operator. For example, Rosenfield and Charney point out that the replacement of allylic axial hydrogen atoms by methyl groups increases the magnitude of one-center dipole velocity matrix elements directed along the X axis shown above for 1,3-cyclohexadienes, i.e., essentially along the axial methyl C-C bond axes. The change from positive to negative values for the calculated rotatory strengths listed above is attributed to these increases.[27] These one-center terms $(s|\nabla_X|p_X)$ are the source of Z-polarized components of $\mathbf{m}_{KN}$ projected on the zero-order "allowed" μ_{NK} when "Kirkwood terms"[14] depending on $\mathbf{R} \times (i|\nabla|j)$ are dominant. A geometrical bias for the importance of the ∇_X over the ∇_Y component of such terms arises when the methyl groups are close to, but not on the YZ plane so that the Y component of their coordinate location is large compared to the X component. These are the geometrical characteristics of the methyl-substituted 1,3-cyclohexadienes that were considered. The important one-center terms arise from the mixing of s and p_X methyl carbon atom orbitals into the two SCF molecular orbitals that are singly occupied in a single-configuration approximation to the excited state.

It is common practice to improve molecular orbitals to the self-consistent field (SCF) level of accuracy, hoping for sufficient consideration thereby of electron correlation so that any CI refinement can be neglected. Indeed the single-excitation CI refinements of SCF treatments for rotatory strength seem to yield a paradoxical "excess of sufficiency". It has been found that when molecular wave functions were improved beyond the SCF-MO approximation by the introduction of CI, an instance where the coefficients to additional terms for s and p_X methyl carbon atom orbitals *can* be explicitly related to dynamic coupling (and static coupling), results for rotatory strength that were incorrect in sign and generally arbitrary were obtained.[27] A number of other authors have excluded consideration of similar limited, single-excitation CI so as to maintain agreement with experiment.[54] Yet, quantum theory of molecular electronic structure assumes that the inclusion of enough CI can sufficiently improve molecular wave func-

tions that arise from even a poor basis set of non-SCF molecular orbitals.[55]

On the other hand, the random phase (RP) approximation for CI does yield satisfactory, well-behaved oscillator strengths and rotatory strengths.[56] The RP approximation, which includes doubly excited configurations, has been described as a balanced, consistent first-order theory in electron correlation. Moreover, its results do seem to transcend to a large degree the choice of molecular orbital basis set.

Now let us depart from our original assumption that the molecular wave functions $|A_r\rangle$ and $|B_s\rangle$ are "exact" spectroscopic state wave functions for separated A and B systems. Let them now represent Salter determinants of SCF molecular orbitals of A and B, or even molecular wave functions improved by sufficient CI within the respective MO manifolds of A and B. Assuming no differential overlap between A and B eliminates consideration of exchange and antisymmetrization between A and B. Then the coefficients to the terms of eq 4b are seen to embody the double excitations of the ground-state configuration balanced against the single excitations of the excited state configuration that characterize the RP approximation for CI-improved transition matrix elements.[56,57] The amplified sector rule thus has a theoretical basis (at the level of perturbation theory) consistent with recent computational advances for the inclusion of CI.[58]

The coupled equations of the RP approximation,[57] not unlike those for vibrational normal coordinate modes and frequencies, will accommodate with rigor the characteristics of perturber nonadditivity and polarizability exaltation on approaching a resonance with the chromophore transition. In more restricted forms neglecting intersystem overlap we obtain the methods of linear response theory[51,59] and Green's function methods,[60] methods that are still able to represent these characteristics with precision.

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Vibrational Analysis by Electron Paramagnetic Resonance Spectroscopy. The Isopropyl Radical[1]

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Abstract: The isotropic hyperfine interactions of the protons and the α carbon atom of the isopropyl radical have been measured by EPR spectroscopy over the temperature range 130–350 K in liquid isooctane or propane. The data fit extremely well to a hypercotangent function of temperature derived on the assumption that a single, simple harmonic oscillator, the out of plane vibration of the radical, modulates the isotropic coupling constants. A vibration frequency of 380 ± 12 cm^{-1} deduced from the results is in excellent accord with the infrared spectroscopic value. INDO molecular orbital calculations predict hyperfine interactions and their dependences on the out of plane angle which are in fair agreement with the experimental observations.

Introduction

Modern experimental EPR techniques permit the observation of practically any thermodynamically stable radical even though it is kinetically transient,[2] and yield isotropic coupling constants which lead directly to structural information on free radicals. By contrast, gas-phase ultraviolet, photoelectron spectroscopic, and matrix isolation infrared methods provide detailed information about the vibrational behavior of radicals. They generally provide less structural information and are often limited experimentally because of the difficulties associated with radical generation.

It would clearly be advantageous, for experimental reasons,

if the EPR technique could be used to provide vibrational information. This is possible, in principle, for a mode in which the isotropic coupling constants are strongly dependent on vibrational energy. Measurement of the temperature dependence of the coupling constants over a temperature range appropriate to the vibrational frequency in such a case should yield information about that particular mode, such as the frequency and the EPR parameters for radicals in vibrationally excited states.[3]

Such possibilities for the application of EPR have been recognized for some time.[4] For example, methyl has been studied to a limited extent[5] experimentally[7,8] while *tert*-butyl,[9] 7-norbornenyl,[10] some aromatic anions and cations,[11] and

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